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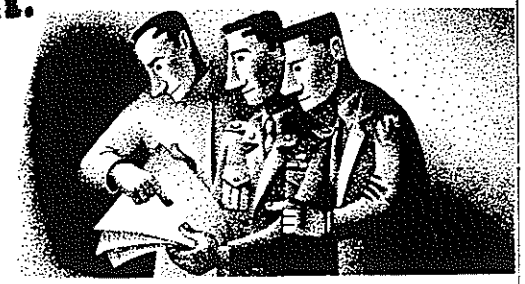
DEVELOPING A BLACK PEPPER SUBSTITUTE



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***Much of the work done at the Quartermaster Research and Development Laboratories, Philadelphia, Pa., is directly or indirectly related to the food and container fields. The following article is the first of a series planned to describe developments at the Philadelphia Laboratories of interest to readers of the* Activities Report.**

The development of a synthetic pepper, undertaken for the QMFCI by the Pioneering Research Division of the QM R and D Laboratories, is a virtually completed project of strategic military importance owing to the probable unavailability of natural pepper (all of which must be imported) in the event of war. In addition, the existence of a satisfactory pepper substitute made at low cost from domestically available materials may have a considerable influence on the commercial pepper market.

The synthesis of a pepper substitute, as indicated below, is a complex chemical task. It was accomplished by the energy and close cooperation of many individuals and several different research groups. The difficulties of such work are exemplified by the fact that two Nobel prize winners, Staudinger and Reichstein, took more than ten years to define chemically the flavor of coffee; and that three coordinated research groups, two Swiss and one French, worked for twelve years to elucidate strawberry flavors. That a substitute for pepper has been found after only three years of experimentation is a tribute to the conscientious and cooperative labors of all who participated in this program.

During the summer of 1949, the Pioneering Division of the Quartermaster Research and Development Laboratories was requested to make a series of peppery-bite chemicals for the Quartermaster Food and Container Institute. Upon completion of this work the following spring, the laboratories were assigned the problem of providing the background for the formulation of black pepper substitutes from domestic raw materials. This project was undertaken to forestall a shortage of black pepper in the event of a national emergency.

pepper's pedigree

During World War II, the interesting observation was made that about 20 per cent of the less expensive meat cuts were rejected by

the soldiers when black pepper was not available. Due to enemy action, the import of this spice of the East Indies was made impossible. Whether pepper is actually necessary in foods has not as yet been scientifically established. It is known, however, that pepper is a Quartermaster item of long standing. The Roman soldiers more than two thousand years ago obtained a daily allowance of pepper. In the sack of Rome in the year 410 A.D. by Alaric the Goth, a part of the ransom consisted of three thousand pounds of black pepper. A more convenient route to the "Spice Islands" was the primary objective of Columbus' journey. It is also of interest to recall that the City of Philadelphia, through the good offices of Benjamin Franklin, provided each of the officers of Braddock's ill-fated campaign, during the French and Indian War, with one-half pound of pepper.

background and objectives

In planning the Quartermaster project on the development of a black pepper substitute, first consideration was given to a clear definition of objectives. While the active principles of the natural product have been described and synthesized, the composite natural product has never been duplicated: vanillin *vs.* the vanillabean, cyclic polymembered ketones *vs.* musk, ionone *vs.* essence of violets, etc. The human sense of smell and taste is apparently able to distinguish a substitute from the natural product when the comparison is made *per se,* but not so readily in mixtures. This concept permitted the definition of our objective: a black pepper substitute that cannot be detected as a substitute when used in foods, because it has no deleterious effect on their flavor as compared with natural pepper; and that resembles *per se* the natural spice as nearly as possible when compared directly.

The first requisite is absolute; the second is elastic and abstract without a set standard. Thus it developed that the main objective of our research task was to establish how close the imitation could be brought to resemble the natural product within the set Quartermaster limitations of the project, that is: "to formulate a black pepper substitute from domestically available raw materials."

Imitation black peppers are not new. In Germany during World War I, beta-cinnamenyl acryloyl piperidide and 5-phenyl-n-valeroyl piperidide were employed as synthetic peppery-bite chemicals, mixed with flour and flavored with phellandrene. In World War II, beta-cinnamenyl acryloyl-piperidide alone was used as the synthetic pungency chemical by the Germans, because according to Staudinger, the inventor, it showed itself superior to the natural black pepper alkaloid, piperine, for promoting digestion of carbohydrates.

Domestic imitation black pepper now available contains the oleoresin of capsicum of red pepper as the biting ingredient, flavored with terpenes and extract of natural black pepper on a flour filler. Some manufacturers extend their product with natural black pepper spice.

It can be said that both the German and the domestic imitations fulfill the requisite "of not having a deleterious effect on the flavor of foods, as compared with natural pepper." The German imitation has a bite not detectable from natural piperine. Capsicum has a bite different from piperine—the heat sensation occurs in the throat, and not on the tongue, as experienced by everyone who has eaten Mexican food. The German pepper substitute does not fulfill the requisite of resembling the natural spice *per se.* It has an odor of turpentine, since the phellandrene used as the flavoring material originates from the terpene fraction of eucalyptus oil.

The domestic imitation black peppers fulfill the general requisite for a substitute. However, they do not fulfill the Quartermaster requirement to be made from domestically available raw materials. While considerable quantities of red pepper are grown on this continent, the main volume of capsicum is imported from French Algiers. Caryophyllene is a by-product of clove oil refining, which comes from

equatorial Africa. Natural black pepper is grown in the East Indies only.

The German imitation pepper may be regarded as a true black pepper substitute since the synthetic bite chemical is a homolog of piperine. The present domestic imitations are not. They are imitation red peppers modified to resemble black pepper, since they contain the oleoresin of this spice as the main bite chemical.

planning the program

With these considerations in mind, the research program was planned and the subtasks defined after completion of the exploratory phase, which, in this case, was of short duration.

Based on the assumption that flavor is the sum of the sensory responses of odor, taste (pungency) and texture, the natural spice was separated into volatile pepper oil, the odor component; odorless oleoresin responsible for pungency and a tasteless and odorless pulp constituting the filler responsible for the texture of the spice. On recombining the components (volatile oil, odorless oleoresin and inert pulp) in the proportion as they appear in natural pepper, a product was obtained which differed in flavor from the natural spice.

The experience was of significance since it showed that in the work ahead, we could not rely on chemical methods and physical instrumentation alone. The elementary analysis of the volatile pepper oil checked within limits of error for terpene hydrocarbons. Keen human range of smell pointed towards the presence of oxygenated compounds, which were not detectable by usual procedures. In consequence, new methods had to be established for the separation and identification of constituents having characteristic odor notes. In addition, modern techniques not yet generally adapted to terpene chemistry were introduced. These novelties, chromatography, the use of Girard's "T" reagent, spectrophotometry, etc., proved to be of value in our work. They also convinced us that an immense amount of research has to be done in order to make them fully useful to flavor chemistry. Large areas of fundamental organic chemistry have to be reworked before we are in possession of reliable infrared spectrophotometric information on pure terpenes and on their oxygenated derivatives, which are responsible for fine odor differences of fruits and vegetables detectable presently only by the sense of smell.

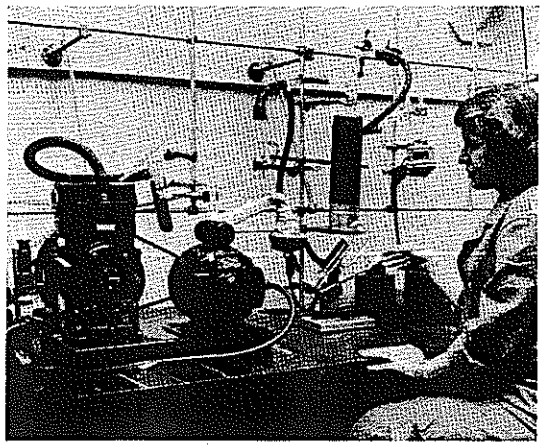
One of the innovations was an olfactory testing panel scientifically trained to locate specific flavor notes. This panel was employed throughout the work as an adjunct to the chemical phase of investigations. We believe that this represents one of the first organized attempts to employ the human sense of smell in the isolation of organic compounds.

The areas of investigation selected as important to the reaching of our objective were as follows:

1. Isolation and identification of the volatile odor principles of natural pepper.
2. Study of synthetic peppery-bite chemicals.
3. Exploratory investigation of natural pepper oleoresin.
4. Study of extracted pepper pulp.

The knowledge gained was then employed in the development of formulations for the imitation spice. Work on these formulations started at an early date and the compositions were improved as soon as new components of the natural product were identified.

Supporting research. The work on the composition of volatile pepper oil, oleoresin, and on the formulation of imitation spice has been carried out on QM research contracts



High vacuum distillation of peppery-bite intermediates.

by the Evans Research and Development Corporation, New York City. Valuable aid in the selection of imitation peppers and in coordination of testing was continuously obtained from Mr. David R. Peryam, of the QM Food and Container Institute. Synthetic peppery-bite chemicals were investigated at the QM Pioneering Research Laboratories. The carbohydrates of the natural spice were not investigated, nor were the synthetic fillers more basically scrutinized, since Staudinger has furnished the basic information relative to the behavior of piperine and synthetic bite chemicals in mixtures with flour.

"building in" odor and bite

As already indicated the characterization of the odor components of the natural spice was by far the most difficult sub-task. Past literature suggested only four components present, none of an oxygenated nature. Now this concept has been entirely changed. Twenty-four new compounds were discovered, including a number of highly characteristic odor notes, consisting of oxygenated terpenes.

It can be said that our knowledge about the volatile pepper oil has been brought up to date. The significance of indirect results should not be overlooked. They consist of both new and improved methods for the isolation and identification of fruit and vegetable flavors.

The study of synthetic peppery-bite chemicals was less difficult. This sub-task was confined to checking the comprehensive results of past investigators and selecting the proper synthetic bite chemical. We shall not dwell on our new findings in this field, since most of the results have been published or are in press. It may be added, however, that new bite chemicals were synthesized by replacing the piperidine with various amines, including vanillylamine, the amine part of capsaicin. The vanillylamine was synthesized by a new procedure from vanilline, originating from newsprint mill waste lignine. The observation was made that the pipecolides and pyrrolidides of the 5-phenyl-pentanoic acids had a pleasant bite, without off-taste, similar to 5-phenyl-n-valeroylpiperidide. The vanillylamine derivatives were powerful irritants and vesicants. All of these chemicals may become of considerable interest if and when the physiological action of spices, for example, as to their role in promoting appetite, is made a subject for investigation.

It may be added that the synthetic peppery-bite chemicals and some of their analogs show interesting properties of anti-oxidant activity and antagonism toward microbial growth.

The beta-cinnamenyl acryloyl piperidide was selected as the synthetic peppery-bite material because it did prove its worth in Germany during two World Wars. It is not difficult to make, and the expenditure in chemicals is not exorbitant. Furthermore, this chemical was selected and its preparation carefully checked, in order to avoid the formation of poisonous or other undesirable by-products. This was of importance because the most vicious irritants known to man, such as urushiol of poison ivy, are chemically related to piperine and capsaicin.

The formulation of the synthetic spice has followed strictly the QM requirement—namely, to devise an imitation black pepper which can be made at low cost from domestic raw materials. It is believed that such a product has now been made. This being the case, the assignment of the Pioneering Research Laboratories is about completed.

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